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LOW TEMPERATURE PULSED PLASMA DEPOSITION

PART 2 : THE PRODUCTION OF NOVEL AMORPHOUS COMPOUNDS
OF GERMANIUM IN THIN FILM

by

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LOW TEMPERATURE PULSED PLASMA DEPOSITION

PART 2: THE PRODUCTION OF NOVEL AMORPHOUS COMPOUNDS OF GERMANIUM

IN THIN FILM

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ABSTRACT

Recently a new process for the room temperature, low pressure, deposition of thin films has been published, which uses pulsed radio-frequency discharges of very high power levels. Here we describe the use of the process for the deposition of amorphous compounds containing germanium, sulphur, and phosphorus. The deposited compounds, many of which cannot be readily deposited using any other method, are shown to have useful properties as infra-red coatings and as compound semiconductors with band gaps extending into the visible spectrum. The stability of the deposited compounds on exposure to high temperatures and on exposure to moisture is found to correlate with deposition conditions and compound stoichiometry, and the use of these materials under adverse environmental conditions is discussed.



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INTRODUCTION

A recent publication [1] describes a novel low pressure pulsed plasma deposition technique, which is characterised by high powered radio-frequency (RF) pulses and a low duty cycle. During the deposition, the energy in each RF pulse is sufficiently high to dissociate the gas completely enabling very high quality films to be deposited, whereas the low duty cycle enables substrate temperatures to remain low. Furthermore, since complete gas exchange occurs between RF pulses, each pulse can have a different gas composition, thus allowing layered structures to be rapidly constructed.

The control over film composition and quality that this new deposition technique affords makes it an ideal tool for fabricating new materials. In this paper, the pulsed plasma production of amorphous germanium compounds of sulphur and phosphorus is described, and data on IR transmission and refractive indices, optical band gap, electrical conductivity and film stability with moisture and temperature, are presented as a function of film composition. In addition, the use of these materials as infra-red transparent coatings is briefly discussed.

EXPERIMENTAL PROCEDURES

Film Deposition

Film deposition was carried out in two capacitively coupled pulsed plasma reactors, hereafter referred to as reactors Alpha and Beta. Reactor Alpha, used for the GeS films, has been described previously [1], but reactor Beta, which was used to deposit most of the GeP and GePS films, will be described here. The important differences between the two reactors are the size,

gas entry arrangement, and pumping speed. In addition, both reactors used a modified RF electrode for this work, designed to give enhanced control of the induced DC bias, and reduce the resputtering and ion damage in deposited films.

Reactor Beta (Fig. 1) consists of a six-way, 100 mm stainless steel cross, with gas flow down from the top and out to the left, electrode entry top and bottom, and a viewing window at the front. Gas pumping is achieved by a roots/rotary combination with a pumping speed of nominally 500 m³/h, with the pumping speed at the chamber controlled by an automatic throttle valve. A capacitive manometer is connected directly to the chamber to record the pressure. Each of eight gas lines feeds onto a short 100 mm diameter manifold, and (following the direction of gas flow) consists of a mass flow controller (MFC_n), a shut-off valve (SV_n), a specific gas volume (VOL_n), and a rapid operation pulsing valve (PV_n). The pulsing valves enable the gas composition in the chamber to be changed within 20 ms or so, but this facility was not used in this work. The electrodes are made of copper, the grounded electrode being uninsulated and entering from the top through a compression fitting in the gas manifold. The water cooled RF electrode (Fig 1 inset) is a hollow cup with a conformal PTFE insulator and a removable top plate with a centred hole. The sample is placed inside the hollow cup facing the hole. The discharge strikes principally in and around the hole such that the film on the sample is formed from species which have diffused from the plasma region into the hollow electrode.

RF power for reactor Beta is supplied by a custom built 50 kW, 40.56 MHz radio frequency generator, with a rise time of less than

1 μ s. Forward and reflected power are measured in the 50 Ω coaxial line leading to the matching box (Plasma Therm), which is of the standard 'L' configuration with two 20 - 750 pF high voltage matching capacitors. At this frequency it is found that the best matching is achieved by replacing the normal coil by a straight copper rod.

Details of the deposition conditions are given in Tables 1 and 2 for the films deposited in reactors Alpha and Beta respectively.

Film Analysis

The compositions of the GeP_xS_y samples were analysed using energy dispersive X-ray analysis in a scanning electron microscope (SEM) with a primary electron beam energy of 5 keV. GaP, ZnS and Ge were used as standards, and results were corrected for absorption and fluorescence of X-rays in the sample. The composition of the GeS_y , and the levels of carbon and oxygen impurities, were analysed using Auger electron spectroscopy. Only trace levels of contaminants were found.

Low angle ($2\theta = 4^\circ - 50^\circ$) X-ray analysis of nominally 1 μ m films on $\langle 111 \rangle$ silicon was performed using a vertical diffractometer and $\text{CuK}\alpha$ radiation.

Infra-red (IR) transmission spectra were obtained over the range 2.5 - 14.7 μ m using a Perkin Elmer model 1750 Fourier Transform IR Spectrometer with a nitrogen purged sample box. Samples, typically 1 - 3 μ m thick, were deposited on 2 mm thick IR grade zinc sulphide substrates. By numerically subtracting the spectrum of the substrate before the deposition from the spectrum of the film and substrate after the deposition, it was possible to avoid spurious signals from contaminants (especially moisture)

in the zinc sulphide. For some samples, the infra-red spectrum was retaken after two simple environmental tests were performed. These were heating in air at 300°C for 1 hour, and immersion in distilled water at room temperature followed by blowing dry with a dry nitrogen gun.

Visible and near IR transmission spectra for absorption edge measurements were obtained using a Varian model 2300 Spectrophotometer, with typically 100 nm thick samples deposited on cleaned glass slides.

RESULTS

Data obtained from films of GeS deposited in reactor Alpha are presented in Fig. 2 and in Table 1. Data on GeP and GePS films are presented in Figs. 3 and 4, and in Table 2. All these films were deposited in reactor Beta, with the exception of those whose IR curves are shown in Fig. 3. X-ray data on samples of compositions 15 and 19 on Si confirmed that the films were amorphous, with broad amorphous peaks centred near $2\theta = 13^\circ$ and 28° ($d = 6.81, 3.19 \text{ \AA}$ respectively). Heating these samples in air at 300° and 400°C resulted in a progressively increasing intensity of the lower angle peak, and intrusion of a sharp peak at $2\theta = 28.5^\circ$ believed to originate from the silicon substrate as the films broke up slightly. Visually, after heating at 300°C the films became speckled, and sample 19 discoloured after heating at 400°C. SEM examination of samples 16 and 19 on silicon showed the films to be featureless in cleaved cross-section (resolution $\approx 200 \text{ \AA}$), though some particles (typically $\geq 1 \text{ \mu m}$) were incorporated.

Before describing the spectroscopic data in detail, a few

general points can be made. Firstly, considerable variation in the interference fringes in the IR spectra can be observed. Because of the lower refractive index of GeS than GeP (nearer the value 2.2 of the ZnS substrates), GeS shows weaker fringes. However, variations in the amplitude of the fringes with wavelength are seen in some samples, which possibly indicates non-uniform optical pathlength through the films and the effects of scattering. Where possible, an estimated value of refractive index has been calculated using the sample thickness, and the wavelengths of interference fringe maxima and their amplitude on the IR curves. For the visible spectra, the relatively high refractive index of the films resulted in strong interference fringes, and this, together with a slow cutoff made it difficult to locate the optical absorption edge accurately. Consequently values quoted in the tables are for the 5% (GeP_xS_y) or 10% (GeS_y) transmission point which were much better defined in these films.

GeS

The IR transmission spectra of a 1.6 μm $\text{GeS}_{1.62}$ film is shown in Fig. 2a., together with the spectra obtained after heating this sample in air at 300°C for 1 hr. A few small absorption peaks are superimposed upon the fringes. The 'noise' in the region of 3500 cm^{-1} and 1600 cm^{-1} is due to residual water vapour in the spectrometer. Heating at 300°C can be seen largely to remove two small hydride peaks but result in a small oxide peak. A refractive index of $n = 2.7 \pm 0.2$ is consistent with the interference fringe data.

In Fig. 2b are shown the IR curves of a similar GeS sample

before and after a 1 hr and an 18 hr immersion in distilled water. As well as showing small hydride peaks, the spectra of the sample as deposited shows a very small C-H peak, believed to originate from COS impurity in the H₂S gas. Two other small peaks at 1400 and 1050 cm⁻¹ are unidentified, but these peaks are lost after immersion, suggesting that they may result from surface contaminants. Immersion of the sample also results in the formation of two small oxide peaks at 1600 and 750 cm⁻¹, corresponding to O-H and Ge-O bonds respectively.

The variation of the 10% optical transmission point in GeS_y as a function of composition is shown in Table 1. By controlling the ratio of GeH₄ to H₂S in the reactor, it is possible to obtain values from 790 nm (Ge rich) to 430 nm (S rich) in an approximately linear progression. Heating the samples in air at 260°C for 48 hours consistently lowers these values by about 30 nm.

GeP and GePS

Fig 3a shows the IR spectra of an $\approx 2 \mu\text{m}$ GeP_{1.97} thick film before and after a 1.5 hr immersion in distilled water. Neither curve shows any major peaks, except a small one at 2200 cm⁻¹ which is little affected by the immersion treatment. The main effect of the immersion is to displace the thickness fringes sideways, consistent with an optical pathlength (nd) increase of 2.4%. In Fig. 3b are shown the IR curves obtained from a nominally identical sample before and after room temperature ageing for 100 days and no significant change in the IR spectra occurs.

The deposition conditions, compositions and band edge

wavelengths of a series of GeP_xS_y films are given in Table 2. Three of these compositions (marked *) were also prepared as nominally 3 μm thick IR samples and the resulting IR curves are shown in Fig. 4. Fig. 4a shows the IR curves of the first of these samples, $\text{GeP}_{1.13}$, before and after heating at 300 °C for 1 hour. Before heating the film was very soft and had a sooty-black appearance, and this together with the lack of interference fringes and the general appearance of the IR spectrum suggests a high scattering inhomogeneous film. After heating a very large oxide absorption band covers the whole of the 1200 - 900 cm^{-1} region. IR spectra for a $\text{GeP}_{3.50}$ sample, as deposited, after heating at 300°C, and after subsequent water immersion, are shown in Fig. 4b. Heating results in the loss of several small hydride and oxide peaks (indicating the latter may result from surface contamination), an increase in the amplitude of the interference fringes and a displacement of their position consistent with a decrease in optical pathlength of $\approx 5\%$. The estimated refractive index before heating is $n = 3.1 \pm 0.2$. Water immersion slightly further enhances the interference fringes and their displacement, and removes a remaining small (presumably surface) oxide peak.

The behaviour seen in the IR curves of $\text{GeP}_{0.88}\text{S}_{1.02}$, shown in Fig. 4c, is in some respects similar, with heating at 300°C removing several small hydride peaks but here resulting in (presumably) surface oxide which is lost with immersion in water. Heating again causes displacement of the interference fringes, consistent with an optical path decrease of $\approx 3.3\%$. Initially the refractive index is $n = 2.9 \pm 0.2$.

The variation of the 5% optical transmission point for the

GeP_xS_y films shown in Table 2 is from 870 nm for Ge to 500 nm for GeP_{0.88}S_{1.02}, generally decreasing as more sulphur or phosphorus is added. Heating at 300°C for 1 hour lowers the 5% transmission point by 50-100 nm, the slightly higher values near stoichiometric GeP. Before heating the width of the absorption edge (5%-95% transmission) ranges from about 900 nm for Ge rich samples, to 450 nm for very P/S rich samples. After heating this width decreases slightly, the respective figures then being 700-350 nm.

Crude resistance testing was performed on the GeP_xS_y samples, using a multimeter with probes placed \approx 2 mm apart, a voltage of 1.8 V, and a resistivity full scale of 20 M Ω . Samples 11 - 21 all showed resistivities $>$ 20 M Ω (ie. over full scale) at room temperature. At \approx 250°C, samples 11, 12, 13 and 21 showed resistances of \approx 3 M Ω , 0.3 M Ω , 5 M Ω , and 10 M Ω respectively, all other samples remaining over full scale.

Further electrical testing using a ceramic mounted 4 point probe (point spacing 3.2 mm) on a heated stage and a 100V, 0-1 μ A constant current source is in progress. Linear plots of $\ln(\text{voltage})$ against $1/T$ have been obtained, from which values of the band edge consistent with the optical data presented here have been calculated.

DISCUSSION

It is clear from the data in Tables 1 and 2 that the pulsed plasma deposition technique is able to form compounds with a very wide range of compositions. The low temperature of the deposition process enables compounds to form which are not thermodynamically stable, and hence are difficult to make by any other method. In

this section we compare the results obtained here with the results from other workers using more conventional techniques of synthesis.

Data on the GeS and GePS systems is fairly readily available and a large glass-forming region is known to exist in the P/S rich corner of the ternary phase diagram [2-5]. Measurements of the optical band edge of bulk glassy samples in the range GeS to GeS₂ have previously been reported by Kawamoto [5].

There is much less data available on the binary system GeP_x since this system is difficult to prepare by conventional means because of the peritectic melting of GeP [6] and the high volatility of phosphorus. Thin amorphous films of (near) stoichiometric GeP have previously been prepared by evaporation [7] from a monocrystalline GeP source, and analysis has suggested that their local order is similar to that of the bulk monoclinic phase [8]. The amorphous films were semiconductors with optical band gaps close to the source monocrystalline GeP value of 0.95 eV (= 1.3 μ m), in agreement with the optical data obtained here for sample 13 which is of similar composition. Generally only GeP has been formed by preparation at ambient pressure [9], although electrochemical deposition at 800°C is reported to produce GeP₂ [10]. Under high pressure and temperature other phases can also be produced [11] with compositions near GeP₃ and GeP₅. These phases exhibit metallic conduction and are apparently at least moderately stable subsequently at ambient temperature and pressure.

The data in Table 2 shows that amorphous films of GeP_x can be produced from the plasma with a wide range of compositions ($x = 0.5-7$), and with a corresponding variation in optical behaviour.

The change in the 5% transmission point to shorter wavelengths after heating at 300°C cannot result from loss of phosphorus since it is in the wrong sense, although the films are anticipated to be thermodynamically unstable at relatively low temperatures [12]. The X-ray diffraction data seems to suggest the change in band gap is related to a structural change as the sample is heated. One possibility is the initial formation of a random covalent network structure where heterogeneous Ge-P bonds are not preferred, which changes on heating to a more chemically ordered structure. A change of this type has been suggested to occur in amorphous GeS thin films [13]. A change in bond energy and band gap could also account for the measured decrease in optical pathlength of the IR samples by an associated reduction in the refractive index n .

Several empirical models [13,14] relate, with some success, the mean or minimum band gap to the bond energies in covalently bonded semiconducting crystals, in order to predict the effects of varying composition. The model by Tichy [13] uses a modified version of Manca's [14] relationship, and relates the band gap E_g to the sum of bond energies E_{sj} , each of fraction c_j , by

$$E_g = b(E_s - a) \quad \text{where} \quad E_s = \sum_j c_j E_{sj}$$

and a, b are constants

If band gap behaviour can be generally predicted in this fashion for amorphous semiconductors, then the sense of the change in band gap with annealing could represent the formation of strong bonds at the expense of weaker ones. Heterogeneous Ge-P bonds are clearly energetically favourable over Ge-Ge and P-P bonds in view of the large enthalpy of formation of GeP from the elements (114

kJmol^{-1} , [15]) and hence annealing the deposited films should form more of these bonds and shift the band edge to the blue. This model is supported by the observations made here, where all compositions of the binary and ternary GeP_xS_y are observed to show such a change in absorption edge on annealing. This model also predicts that annealing of as-deposited amorphous films with a random network structure will generally increase the band gap, unless other effects intervene.

The stability of the deposited GeP_x films to the environmental tests appears to improve with increasing phosphorus content, such that $\text{GeP}_{3.50}$ appears fairly stable. Both GeS_y and GeP_xS_y show some oxidation on heating, apparently only at the surface in the ternary system, and binary GeS_y shows some oxidation with immersion in water as has been previously noted for bulk GeS_y glasses [4]. GeP is known to be thermodynamically unstable with respect to the loss of phosphorus at temperatures above 400°C [12], but no such loss was found with the films at the temperatures used here, even with films with a high phosphorus content. Therefore the loss of phosphorus, while thermodynamically allowed, is probably kinetically quite slow.

The compounds prepared here have good infra-red properties over a wide range of the infra-red spectrum and may be suitable for coatings on infra-red optics and windows. For high temperature applications, phosphorus rich germanium phosphide looks particularly attractive since it has a large band gap (which is further improved on annealing) and therefore no free electron absorption, coupled with a reasonable stability to both moisture and heat. However, further work needs to be done on the rate of

loss of phosphorus from these compounds at higher temperatures in order to ascertain the useful working life of such a material. It may also be possible to improve the stability of the material by the addition of small amounts of additional elements (e.g. S,B,Al) and work is under way to investigate this.

CONCLUSIONS

Using the new technique of pulsed plasma deposition, homogeneous amorphous films of GeP_x , GeS_y and GePyS_y have been prepared over a wide range of compositions, and properties such as IR transmission, optical absorption edge, and environmental stability, have been evaluated. Phosphorus-rich $\text{GeP}_{3.50}$, in particular, shows good environmental stability, a reasonably large band gap, and good IR transmission characteristics, making it a potentially useful IR material, although thermodynamic instability at higher temperatures may limit its use. It is suggested, using an existing empirical model, that post-annealing of random amorphous thin film semiconductors can result in an increased band gap, which may be beneficial in IR applications by reducing free electron absorption.

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TABLE 1

GeS_y Films Deposited in Reactor Alpha

Sample No.	Gas Flows	Nom. Composition	Analysis Composition	10% Transmission Point	
				Init.	Aged
1	40/20	GeS _{0.5}	GeS _{0.4}	790	-
2	40/40	GeS	-	780	750
3	40/60	GeS _{1.5}	GeS _{1.5}	740	-
4	40/80	GeS ₂	-	660	630
5	40/100	GeS _{2.5}	-	650	620
6	40/120	GeS ₃	-	630	610
7	40/140	GeS _{3.5}	-	620	580
8	40/180	GeS _{4.5}	-	580	550
9	40/240	GeS ₆	-	430	-

Sample thicknesses 100 nm - 200 nm

Ageing treatment was 260°C for 48 hour in air.

- Measurement not taken.

Deposition Conditions

Plant Alpha, 13.56 MHz RF, 200 μ s pulsewidth, 25 Hz pulse rate, 35 kW forward power, 200 mTorr chamber pressure, gas flows GeH₄/H₂S in sccm as given in table, together with 500 sccm Ar. DC bias potential approx. 200 - 300 V. Nominal film compositions are calculated directly from the gas composition.

The RF electrode had an external diameter of 108 mm, an internal diameter of 86 mm and depth of 20 mm, with a conformal PTFE insulator of external diameter 129 mm. The electrode top plate was 5 mm thick with a centered hole 49 mm diameter.

TABLE 2

GeP_xS_y Films Deposited in Reactor Beta

Sample No.	Gas Flows	Nom. Composition	Analysis Composition	5% Transmission Point	
				Init.	Aged
11	60/0/0	Ge	Ge	870	820
12	40/20/0	GeP _{0.5}	GeP _{0.54}	800	-
13*	30/30/0	GeP	GeP _{1.13}	770	670
14	20/40/0	GeP ₂	-	690	-
15*	15/60/0	GeP ₄	GeP _{3.50}	640	570
16	20/40/0	GeP ₇	-	600	540
17	20/40/20	GeP ₂ S	GeP _{1.50} S _{0.41}	590	-
18	20/30/30	GeP _{1.5} S _{1.5}	-	550	-
19*	20/20/40	GePS ₂	GeP _{0.88} S _{1.02}	500	460
20	40/20/40	GeP _{0.5} S	-	670	-
21	40/20/20	GeP _{0.5} S _{0.5}	-	760	-

Sample thicknesses ($\pm 10\%$)	GeP _x	(samples 11-16)	62 nm
	GeP _x S _y	(samples 17-19)	83 nm
		(samples 20,21)	103 nm

The ageing treatment was 300°C for 1 hour in air.

+ Samples of these compositions were also prepared as $\approx 2 \mu\text{m}$ IR samples, the IR curves being shown in Fig. 4

- Measurement not taken.

Deposition Conditions

Plant Beta, 40.68 MHz RF, 100 μs pulsewidth, 25 Hz pulse rate, 30 kW forward power, 210 mTorr chamber pressure, gas flows GeH₄/PH₃/H₂S in sccm as given in table, together with 500 sccm Ar. DC bias potential approx. 2kV. Nominal film compositions are calculated directly from the gas composition.

The RF electrode had an external diameter of 70 mm, an internal diameter of 60 mm and depth of 23 mm, with a conformal PTFE insulator of external diameter 96 mm. The electrode top plate was 5 mm thick with a centered hole 40 mm diameter.

LEGENDS FOR FIGURES

Figure 1: Schematic of the pulsed plasma reactor beta. The inset shows the RF electrode in detail.

Figure 2: IR Transmission spectra of pulsed plasma deposited films of stoichiometry $\text{GeSi}_{1.62}$ a) before and after heating in air at 300°C for 1 hour and b) before and after immersion in distilled water for 1 hour and 18 hours. For clarity the spectra marked ii) and iii) have been displaced by -20% and -40% respectively

Figure 3: IR Transmission spectra of a pulsed plasma deposited film of stoichiometry $\text{GeP}_{1.97}$ before and after a) immersion in distilled water and b) ageing in air at room temperature for 100 days. For clarity, the spectra marked ii) have been displaced by -20%

Figure 4: IR Transmission spectra of a) $\text{GeP}_{1.13}$ b) $\text{GeP}_{3.50}$ and c) $\text{GePo}_{0.88}\text{Si}_{1.02}$. i) shows the films as deposited, ii) the films after heating to 300°C for 1 hour and iii) after 1 hour immersion in distilled water. For clarity, some of the spectra have been displaced by -20% and -40%, as marked.

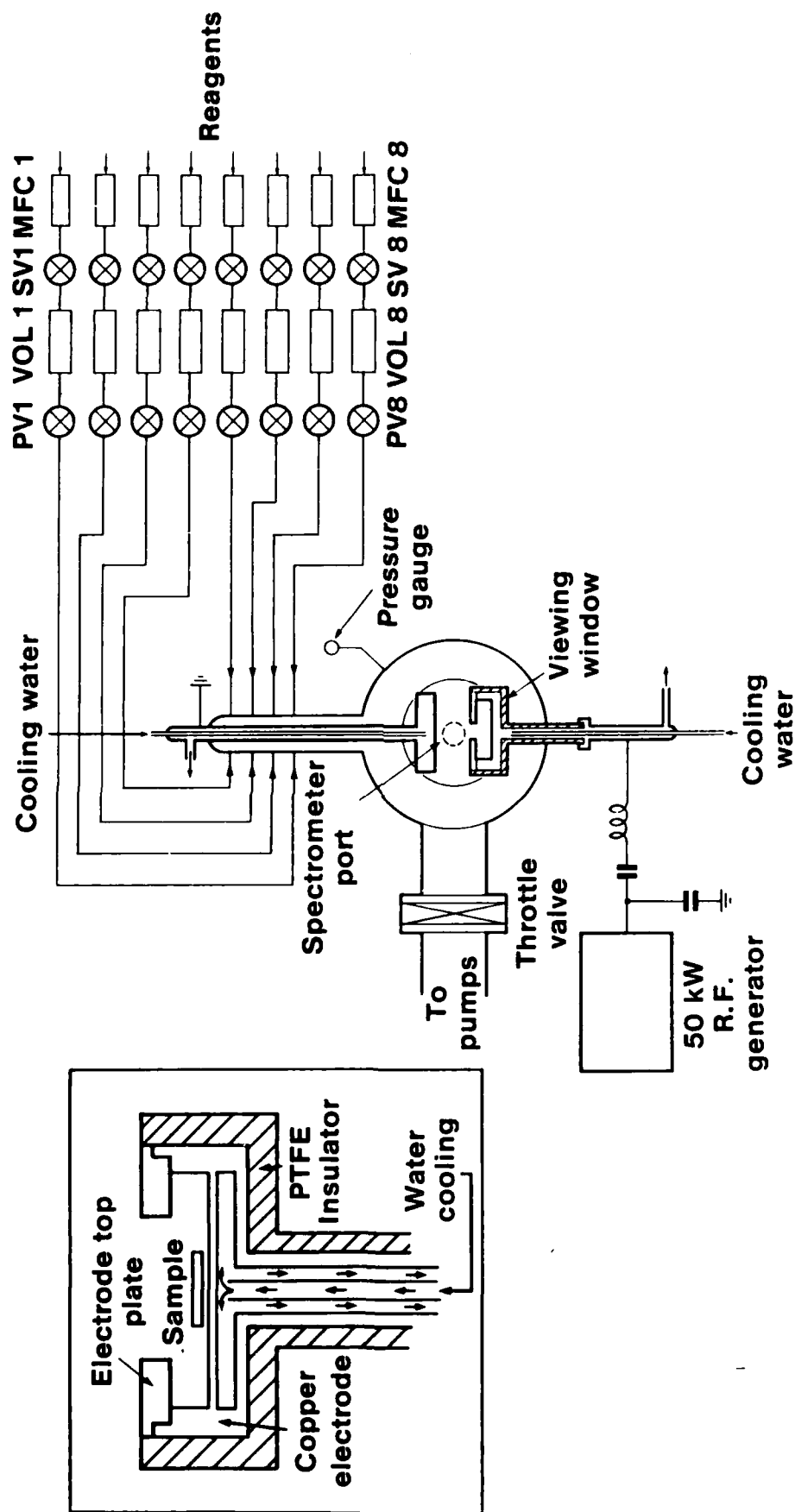
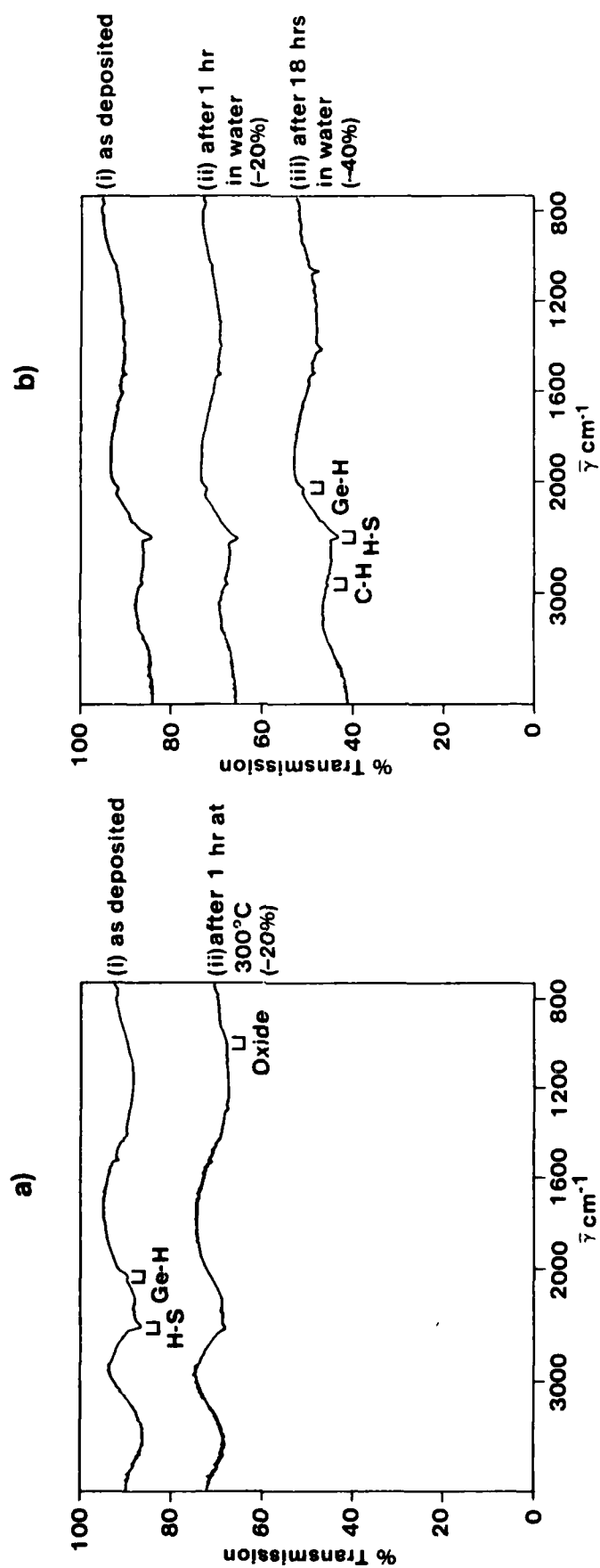


Fig. 1 Pulsed plasma capacitive reactor

Fig. 2 IR Transmission spectra for GeS_{1.62}

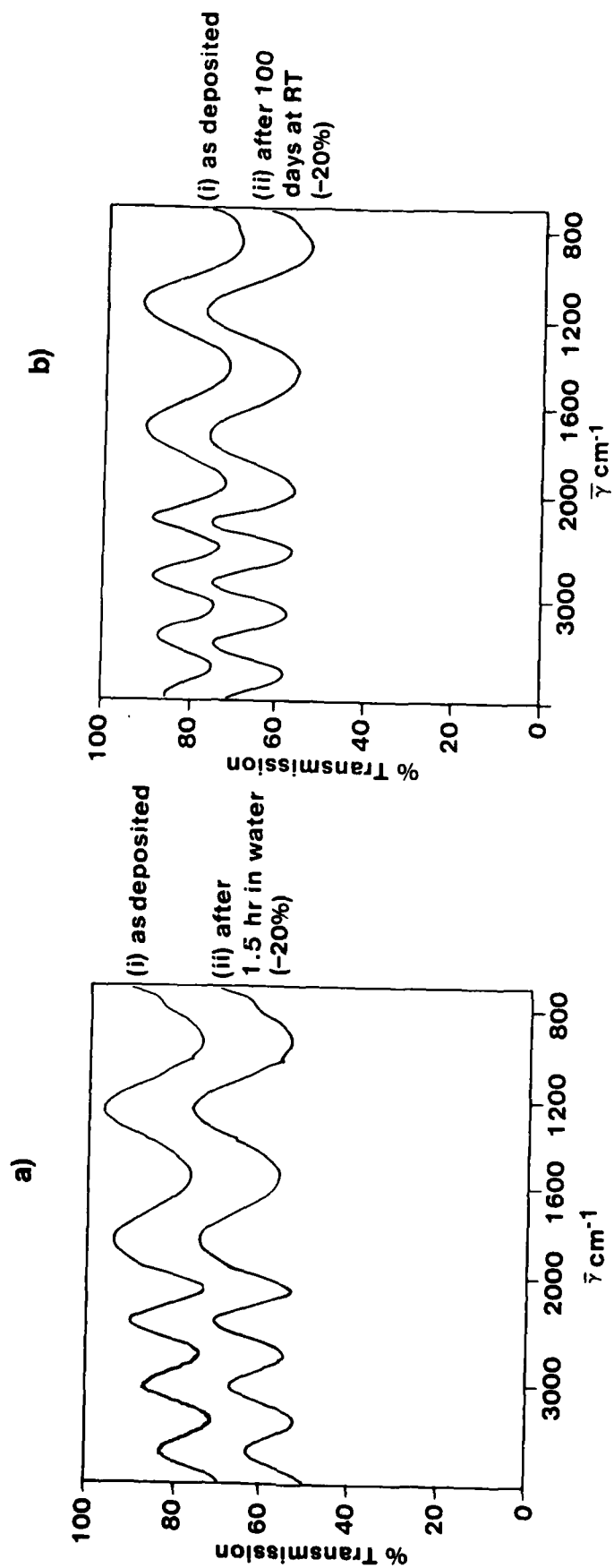


Fig. 3 IR Transmission spectra for GeP_{1.97}

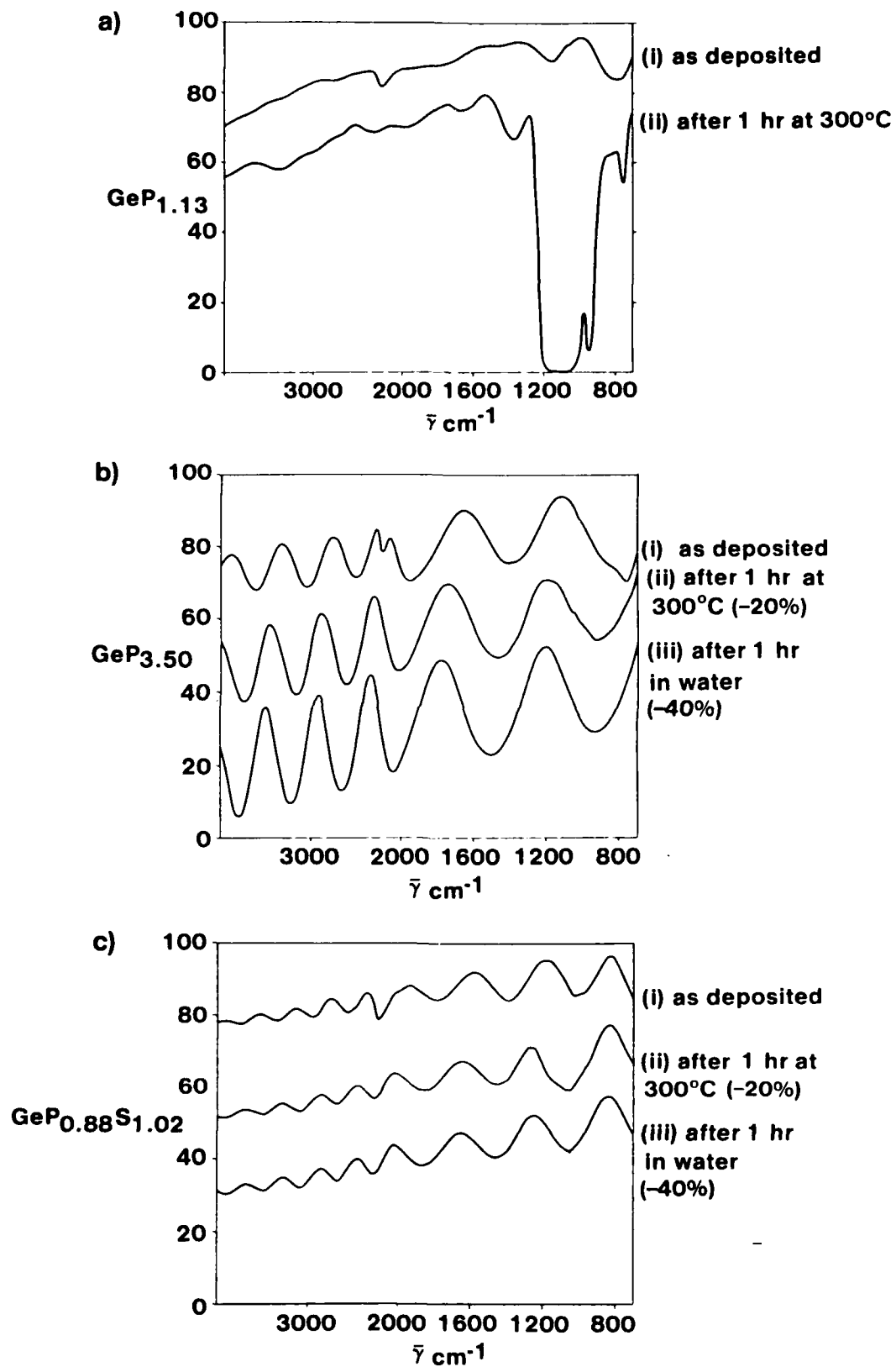


Fig. 4 IR Transmission spectra of GeP_xS_y thin films